

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08L 27/16, C08K 5/14, C09K 3/10 // (C08L 27/16, 27:16)	A1	(11) International Publication Number: WO 98/14517 (43) International Publication Date: 9 April 1998 (09.04.98)
(21) International Application Number: PCT/US97/17607 (22) International Filing Date: 1 October 1997 (01.10.97) (30) Priority Data: 60/028,215 1 October 1996 (01.10.96) US 08/931,141 16 September 1997 (16.09.97) US (71) Applicant: DUPONT DOW ELASTOMERS L.L.C. [US/US]; 300 Bellevue Parkway, Wilmington, DE 19809 (US). (72) Inventor: STEVENS, Ronald, D.; 3921 Nash Boulevard, Norton, OH 44203 (US). (74) Agent: BROMELS, Marilyn, H.; DuPont Dow Elastomers L.L.C., Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
(54) Title: FLUROELASTOMER ALLOY COMPOSITON HAVING EXCELLENT LOW TEMPERATURE PROPERTIES (57) Abstract Peroxide curable fluoroelastomer alloy compositions are provided which, when cured, produce seals having excellent low temperature sealing performance and resistance to volume swell in fuels.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

TITLE

**FLUOROELASTOMER ALLOY COMPOSITION
HAVING EXCELLENT LOW TEMPERATURE PROPERTIES**

5

FIELD OF THE INVENTION

This invention relates to alloy compositions of two or more fluoroelastomer copolymers which are co-curable with peroxides and, in particular, to seals made from these compositions.

10

BACKGROUND OF THE INVENTION

Elastomeric copolymers having interpolymerized units of vinylidene fluoride (VF₂) and comonomers such as hexafluoropropylene (HFP), tetrafluoroethylene (TFE), and perfluoro(alkyl vinyl) ethers (PAVE) are well-known, commercially available materials which exhibit outstanding chemical, thermal and oxidative stability. Fluoroelastomer copolymers which additionally contain iodine or bromine end-groups or copolymerized iodine-containing or bromine-containing cure site monomers are also known. The iodinated or brominated fluoroelastomers may be cured with organic peroxides to produce vulcanizates having excellent tensile strength and compression set properties (see e.g. U.S. Patent No. 4,035,565 and U.S. Patent No. 4,973,633).

The major end use for fluoroelastomers is seals. Because of their chemical stability, fluoroelastomer seals are useful in demanding environments under conditions which cause degradation of seals made from less stable elastomers. For example, shaft seals or o-rings for internal combustion engines must be capable of withstanding exposure to harsh solvents, such as Fuel C and Fuel C/ethanol mixtures, with minimal swelling. Further, leakage must be prevented over temperature ranges which reach at least as low as -40°C. It is difficult to produce a single fluoroelastomer composition economically which has both the required resistance to fuel swell and low temperature leak properties necessary for such end uses.

SUMMARY OF THE INVENTION

The present invention provides fluoroelastomer alloy compositions which may be cured with organic peroxides in the presence of coagents to produce seals
5 which have a leak temperature of less than or equal to -40°C (as described in the Test Method hereinafter) and a fuel swell (168 hours at 23°C in Fuel C) of less than 7 volume percent (as described in the Test Method hereinafter).

The fluoroelastomer composition of this invention comprises a curable alloy formed by blending:

- 10 a) at least two fluoroelastomers, each fluoroelastomer having copolymerized units of vinylidene fluoride and tetrafluoroethylene, and at least one of the fluoroelastomers having copolymerized units of perfluoro(methyl vinyl) ether, wherein the total weight percentage of vinylidene fluoride units, based on the total weight of
15 fluoroelastomers, is 50 to 55; the total weight percentage of tetrafluoroethylene units, based on the total weight of fluoroelastomers, is 10 to 16; and the total weight percentage of perfluoro(methyl vinyl) ether units, based on the total weight of fluoroelastomers, is 20 to 30; each fluoroelastomer having 0.1 to 1.0 weight percent of a halogen
20 selected from the group consisting of bromine and iodine;
 - b) 0.5 to 10 weight percent, based on the total weight of fluoroelastomers, of an organic peroxide; and
 - c) 0.5 to 10 weight percent, based on the total weight of fluoroelastomers, of a peroxide curing coagent;
- 25 thereby producing a composition which, when formed into seals and cured, said seals have a leak temperature of less than or equal to -40°C and a fuel swell, in Fuel C for 168 hours at 23°C , of less than 7 volume percent.

The present invention is further directed to seals such as, but not limited to, shaft seals and o-rings made from the cured fluoroelastomer alloy compositions.

30 Such seals may find use in internal combustion engines.

DETAILED DESCRIPTION OF THE INVENTION

The fluoroelastomer component of the alloys of the present invention comprises at least two fluoroelastomer copolymers. Each of the copolymers includes copolymerized units of vinylidene fluoride and tetrafluoroethylene. In addition, at least one of the copolymers has copolymerized units of perfluoro(methyl vinyl) ether (PMVE). Alloys containing fluoroelastomers having copolymerized units of higher perfluoro(alkyl vinyl) ethers, such as perfluoro(ethyl vinyl) ether and perfluoro(propyl vinyl) ether, exhibit unsatisfactory low temperature sealing performance when formulated into seals. Fluoroelastomers containing higher perfluoro(alkyl vinyl) ethers are therefore not suitable for use in the present invention. The copolymers suitable for use in the present invention may also include copolymerized units of other fluorinated comonomers, including hexafluoropropylene (HFP), 1-hydropentafluoropropylene, 2-hydropentafluoropropylene, and chlorotrifluoroethylene.

Each of the fluoroelastomer copolymer components must be peroxide curable. That is, each fluoroelastomer copolymer must contain about 0.1 to about 1 weight percent bromine or iodine, either as a polymer endgroup or incorporated into the polymer in a cure site monomer, or both. Examples of suitable brominated and iodinated cure site monomers and modifiers include 4-bromo-3,3,4,4-tetrafluoro-butene-1 (BTFB); bromotrifluoroethylene; 2-bromoperfluoro(ethyl vinyl) ether; methylene iodide; 1,4-diiodoperfluorobutane and the like (e.g. U.S. Patent Nos. 5,032,655 and 4,035,565). The composition of each fluoroelastomer copolymer and the relative amount of each copolymer used in the alloy is chosen so that the fluoroelastomer component of the resulting alloy will have a total of 50 to 55 weight percent units of vinylidene fluoride (all percentages are based on the total weight of the fluoroelastomers unless otherwise indicated), 10 to 16 weight percent units of tetrafluoroethylene, and 20 to 30 weight percent units of perfluoro(methyl vinyl) ether. That is, according to the present invention, it is the total amount of vinylidene fluoride units, tetrafluoroethylene units, and

perfluoro(methyl vinyl) ether units present in the fluoroelastomer component of the alloy which is important to attainment of low temperature properties and low fuel swell, not the particular comonomer content of each fluoroelastomer present in the alloy. Preferably the alloy will contain a fluoroelastomer having

5 copolymerized units of hexafluoropropylene, which will be present in amounts of from 5 to 14 weight percent, based on the total weight of the fluoroelastomers. While it is necessary that each fluoroelastomer copolymer contain units of vinylidene fluoride and tetrafluoroethylene, it is not necessary that each copolymer contain hexafluoropropylene or perfluoro(methyl vinyl) ether. Such

10 fluoroelastomer copolymers, and their method of preparation are well known in the art, (see for example, U.S. Patent Nos. 4,035,565; 4,214,060; 4,973,633; 5,032,655; 4,948,852; and 5,077,359, the disclosures of which are hereby incorporated by reference).

The organic peroxide used as a curative in the alloys of the present invention

15 is selected from those peroxides which generate free radicals at curing temperatures. A dialkyl peroxide which decomposes above 50°C is especially preferred. In many cases one will prefer to use a di-t-butylperoxide having a tertiary carbon atom attached to a peroxy oxygen. Among the most useful are 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3 and 2,5-dimethyl-2,5-di(t-butylperoxy)-

20 hexane. Other peroxides can be selected from such compounds as dicumyl peroxide, dibenzoyl peroxide, t-butyl perbenzoate, and di[1,3-dimethyl-3-(t-butylperoxy)butyl]carbonate. Between about 0.1 to 10 wt.%, based on the total weight of the fluoroelastomers, of organic peroxide is used in the compositions of this invention. Preferably, 1 to 3 wt.% is utilized.

25 Between about 0.5 - 10 wt.% (preferably 1-7 wt.%), based on the total weight of the fluoroelastomers, of a peroxide curing coagent which is capable of cooperating with the peroxide to effect a useful cure, such as triallylisocyanurate (TAIC), trimethylallylisocyanurate (TMAIC), tris(diallylamine)-s-triazine, triallyl phosphite, and the like (U.S. Patent No. 5,032,655) is additionally present in the

30 compositions of this invention. Other useful coagents include hexaallyl phosphoramidate, N,N,-diallyl acrylamide; N,N,N',N'-tetraallyl tetraphthalamide;

N,N,N',N'-tetraallyl malonamide; trivinyl isocyanurate; 2,4,6-trivinylmethyl-trisiloxane; and tri(5-norbornene-2-methylene)cyanurate. TAIC and TMAIC are preferred coagents.

A preferred fluoroelastomer blend component of the alloy is a mixture of
5 a) 60-80 weight percent of a fluoroelastomer copolymer having copolymerized VF₂ units, TFE units, PMVE units, and BTFB units with b) 40-20 weight percent of a fluoroelastomer copolymer having copolymerized VF₂ units, TFE units, HFP units, BTFB units and iodine endgroups derived from the chain transfer agent CH₂I₂ which is present during polymerization. A particularly preferred blend is
10 one wherein the first copolymer is a fluoroelastomer having about 54 wt.% VF₂ units, about 10 wt.% TFE units, about 35 wt.% PMVE units, and about 1.2 wt.% units of BTFB, and the second copolymer is a fluoroelastomer having about 50 wt.% VF₂ units, about 20 wt.% TFE units, about 29 wt.% HFP units, about 0.6 wt.% BTFB units and an iodine content of about 0.2 wt.%.

15 The fluoroelastomer alloys of the present invention are prepared by blending together two or more fluoroelastomer copolymers, an organic peroxide curing agent, and a coagent for the peroxide. Blending will be carried out most generally in a Banbury mixer, internal mixer, or on a rubber mill.

The fluoroelastomer alloy composition may also include other well known
20 additives useful in rubber compounding, for example fillers, such as carbon black, non-fibrillating fluoropolymers, clay, silica, talc, metal oxides, divalent metal hydroxides, calcium carbonate, pigments, antioxidants, stabilizers and the like; plasticizers such as dibutylsebacate, dioctylphthalate and the like.

In order to fully develop their physical properties, shaped fluoroelastomers
25 are generally cured. Typically, curing is carried out by heating the composition for about 1-60 minutes at about 150°-200°C. Conventional rubber curing presses, molds, extruders, and the like provided with suitable heating and curing means can be used. Also, for maximum heat resistance and dimensional stability, it is preferred to carry out a post curing operation wherein the molded or extruded
30 article is heated in an oven or the like for an additional period of about 1-48 hours, usually from about 180°-300°C.

The fluoroelastomer alloy compositions of the invention are useful for producing o-ring seals, for use in fuel, lubricant and hydraulic systems, and in automotive shaft seals. They are particularly suited for formulation into seals which are used in low temperature environments. Cured seals produced from the

5 fluoroelastomer alloy compositions of the present invention have a leak temperature of less than or equal to -40°C and a fuel swell, in Fuel C for 168 hours at 23°C , of less than 7 volume percent, preferably less than 6.5 vol.%.

EXAMPLE

10

Test Methods

The following test methods were used to measure various properties reported in the Example and in the claims.

	Mooney Viscosity	-	ASTM D 1646
15	Tensile Strength	-	ASTM D 412
	Elongation at break	-	ASTM D 412
	Hardness, Shore A	-	ASTM D 2240
	Compression set	-	ASTM D 395,
			Method B, plied disks
20	Fuel Immersion Volume Swell	-	ASTM D 471

TR- 10°C and Leak Temperature - R.D. Stevens, E.W. Thomas, J.H. Brown and W.N.K. Revolta in SAE Technical Paper Series #900194 "Low Temperature Sealing Capabilities of Fluoroelastomers", 1990

EXAMPLE

25 Fluoroelastomer Copolymer A ("A") was a tetrapolymer containing copolymerized units of VF_2 , TFE, PMVE, and BTFB units in a weight ratio of about 54:10:35:1.2 The copolymer was prepared according to the emulsion polymerization process disclosed in U.S. Patent 4,035,565 and had a Mooney viscosity, ML-10 (121°C) of approximately 85.

30 Fluoroelastomer Copolymer B ("B"), was a tetrapolymer containing copolymerized units of VF_2 , TFE, HFP, and BTFB units in a weight ratio of about 50:20:29:0.6 The copolymer contained about 0.2 wt.% iodine, had a Mooney

viscosity, ML-10 (121°C) of 25, and was prepared according to the emulsion polymerization process disclosed in U.S. Patent 4,973,633.

Peroxide co-curable fluoroelastomer alloy compositions of this invention and controls of peroxide curable compositions of Fluoroelastomer Copolymer A (Control A) and of Fluoroelastomer Copolymer B (Control B) were prepared by
5 mixing the ingredients shown in Table I in a Banbury mixer. The compositions of Table I were molded into 75 mil (1.9 mm) thick 3-inch x 6-inch (7.6 cm x 15 cm) slabs and press cured at 177°C for 10 minutes under greater than 20 tons (276 MPa) pressure, followed by a post cure at 232°C for 24 hours in an air oven. The
10 physical properties were measured by the above test methods and are reported in Table I. O-rings were prepared, in the same manner as the slabs, for TR-10 and leak temperature testing. As can be seen from the test results, the cured slabs prepared from samples 1-3 of the invention have excellent physical properties, particularly Fuel Volume swells of less than 7 vol.%. O-rings had leak
15 temperatures of -40°C or less.

TABLE I

Component ¹	Control A	Control B	Sample 1	Sample 2	Sample 3
Fluoroelastomer A	100	-	80	70	60
Fluoroelastomer B	-	100	20	30	40
Plasticizer	1	1	1	1	1
Octadecylamine	0.25	0.25	0.25	0.25	0.25
Carnauba Wax	-	0.5	-	-	-
ZnO	3	3	3	3	3
MT Carbon Black	30	30	30	30	30
TAIC ²	2.5	3	2.5	2.5	2.5
Peroxide ³	2.5	3	2.5	2.5	2.5
Physical Properties					
Tensile Strength, T _B (MPa)	22.0	19.8	20.0	18.5	17.3
Modulus, M ₁₀ (MPa)	0.7	-	0.8	0.8	0.8
Modulus, M ₁₀₀ (MPa)	5.0	5.8	4.7	4.5	4.7
Compression Set, (%), 70 hr @ 200°C	29	41	33	35	34
Elongation at Break, E _B (%)	240	233	240	230	220
Hardness, Shore A (pts)	69	77	72	72	72
TR-10 (°C)	-30.3	-16	-27	-26	-24.4
Leak Temperature, °C	-44	-30	-42	-40	-40
Fuel C Swell (Vol. %)	7.8	4.5	5.5	5.9	5.9

¹Parts by Weight²Triallylisocyanurate³2,5-dimethyl-2,5-di(t-butylperoxy)hexane

CLAIMS:

1. A fluoroelastomer composition comprising a curable alloy formed by blending:

- 5 a) at least two fluoroelastomers, each fluoroelastomer having copolymerized units of vinylidene fluoride and tetrafluoroethylene, and at least one of the fluoroelastomers having copolymerized units of perfluoro(methyl vinyl) ether, wherein the total weight percentage of vinylidene fluoride units, based on the total weight of
10 fluoroelastomers, is 50 to 55; the total weight percentage of tetrafluoroethylene units, based on the total weight of fluoroelastomers, is 10 to 16; and the total weight percentage of perfluoro(methyl vinyl) ether units, based on the total weight of fluoroelastomers, is 20 to 30; each fluoroelastomer having 0.1 to 1.0 weight percent of a halogen
15 selected from the group consisting of bromine and iodine;
- b) 0.5 to 10 weight percent, based on the total weight of fluoroelastomers, of an organic peroxide; and
- c) 0.5 to 10 weight percent, based on the total weight of fluoroelastomers, of a peroxide curing coagent;
- 20 thereby producing a composition which, when formed into seals and cured, said seals have a leak temperature of less than or equal to -40°C and a fuel swell, in Fuel C for 168 hours at 23°C, of less than 7 volume percent.

2. The composition of Claim 1 wherein at least one fluoroelastomer has copolymerized units of vinylidene fluoride, tetrafluoroethylene, and
25 hexafluoropropylene.

3. The composition of Claim 1 wherein the organic peroxide is 2,5-dimethyl-2,5-di(t-butylperoxy)hexane.

4. The composition of Claim 1 wherein the organic peroxide is present in an amount of from 1-3 wt.%, based on the total weight of
30 fluoroelastomers.

5. The composition of Claim 1 wherein the coagent is selected from the group consisting of triallylisocyanurate and trimethylallylisocyanurate.

6. The composition of Claim 1 wherein the peroxide curing coagent is present in the amount of from 1-7 wt. %.

5 7. The composition of Claim 1 wherein the fluoroelastomer component of the curable alloy is composed of

a) 60-80 weight percent of a fluoroelastomer having copolymerized units of vinylidene fluoride, tetrafluoroethylene, perfluoro(methylvinyl) ether and 4-bromo-3,3,4,4-tetrafluorobutene-1; and
10

b) 40-20 weight percent of an iodinated fluoroelastomer having copolymerized units of vinylidene fluoride, tetrafluoroethylene, hexafluoropropylene, and 4-bromo-3,3,4,4-tetrafluorobutene-1.

8. The composition of Claim 1 wherein at least one of the
15 fluoroelastomers comprises copolymerized units of a comonomer selected from the group consisting of 4-bromo-3,3,4,4-tetrafluorobutene-1; bromotrifluoroethylene; and 2-bromo-perfluoro(ethyl vinyl) ether.

9. A seal formed from the cured alloy of Claim 1.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/17607

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08L27/16 C08K5/14 C09K3/10 //(C08L27/16,27:16)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08L C08K C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 06 329 860 A (ASAHI GLASS CO LTD) 29 November 1994 see examples 1-3	1,2,4-6
A	EP 0 600 090 A (ASAHI CHEMICAL IND) 8 June 1994 see claims; example 7	1,9



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

20 January 1998

Date of mailing of the international search report

03/02/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

DE LOS ARCOS, E

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 97/17607

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 06329860 A	29-11-94	NONE	
EP 0600090 A	08-06-94	US 5374484 A	20-12-94
		CA 2103677 A	12-11-93
		WO 9323469 A	25-11-93
		JP 6157686 A	07-06-94